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Magnetocrystalline anisotropy energy in cubic Fe, Co, and Ni: Applicability of local-spin-density theory reexamined

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We report an *ab initio* investigation of the magnetocrystalline anisotropy energy (MAE) in bcc Fe and fcc Co and Ni. We introduce the spin-orbit scaling (SOS) technique, which, in combination with the force theorem, we use to achieve numerically converged MAE's. From these MAE's, and from MAE's which we separately obtain from total energy calculations, we investigate the ability of energy band theory based upon the local-spin-density approximation to describe the MAE in the cubic $3d$ metals. The SOS technique yields the correct easy axis for Fe and Co, but a vanishing MAE for Ni. Our total energy calculations on a smaller number of 3.7×10^5 k points predict the correct easy axis in Fe, Co, and also Ni. [S0163-1829(98)03716-3]

The problem of the magnetocrystalline anisotropy energy (MAE) in the ferromagnetic $3d$ metals Fe, Co, and Ni is one of the longest standing and still incompletely solved problems in the field of metallic magnetism.[1–5] The MAE, which is the energy that directs the magnetization along a certain crystallographic axis, called the easy axis, is in the cubic $3d$ transition metals a very small quantity of only a few μeV/atom.[6–8] Nonetheless, the MAE is the source of the permanent ferromagnetism in Fe, Co, and Ni. In addition, the MAE causes the (001) axis to be the preferential magnetization axis in bcc Fe, but the (111) axis in fcc Ni, a curiosity which naturally attracted attention.

Already many years ago, a first theory of the MAE in Fe and Ni was formulated by Brooks[1] and Fletcher,[2] who emphasized that an energy band picture, in which the effect of spin-orbit coupling (SOC) is taken into account in a perturbative way, could provide a coupling of the magnetization orientation to the crystallographic axes of approximately the right order of magnitude. In this pioneering work the bandstructure was oversimplified to three empirical bands.[1,2] Recent investigations[3–5] elaborated the MAE problem using *ab initio* calculated energy bands obtained within the local-spin-density approximation (LSDA) to density functional theory. Although it is beyond doubt that LSDA energy bands are superior to empirical bands, it turned out that calculating the MAE from first principles poses a great computational challenge. The prime obstacle is the smallness of the MAE of only a few μeV/atom, a value which ought to result as the difference of two total energies for different magnetization directions, which are both of the order of $4\,10^4$ eV/atom. Owing to this numerical problem, it remained at first unclear if the LSDA could at all describe the MAE correctly, since the wrong easy axis was obtained for hcp Co and fcc Ni.[3] Recent contributions aimed consequently at improving the numerical techniques,[5,9] with the result that the correct easy axis was obtained for hcp Co, but not for fcc Ni.[5] Obviously, this particular MAE difficulty is imposed by the cubic crystal symmetry, whereby the magnetic anisotropy is extremely reduced in magnitude. Already in hcp Co[6] the MAE is almost two orders of magnitude larger than in fcc Co,[7,8] and even larger MAE's of meV/atom occur in thin transition metal films.[9–11]

In the present work, we reexamine the fundamental issue whether LSDA energy band theory can describe the MAE in the cubic $3d$ metals. Previously the MAE problem was addressed in first-principles calculations using either the force theorem to compute the MAE,[3] or the total energy.[5] Each of these approaches has its specific advantages and disadvantages. It was found that when employing the force theorem, the calculated MAE depends delicately on the k-point mesh in the Brillouin zone (BZ).[3] In addition, it was criticized quite recently that the force theorem in itself is an approximation for evaluating the MAE in cubic materials.[12] Thus, MAE's computed using the force theorem can differ from those computed from total energies. In order to examine the MAE problem as accurate as possible, we have chosen to apply both approaches to evaluate the MAE's. In the following we shall first consider the convergence of MAE values obtained with the force theorem with respect to the k-point mesh. From the requirement that the BZ mesh employed must sufficiently resolve those parts in the BZ where, e.g., SOC lifts band degeneracies, a homogeneous mesh of at least 10^7 k points in the whole BZ can be inferred. Such an amount of k points, however, is unmanageable due to the present-day existing computational limitations. We therefore introduce a new technique, the spin-orbit scaling (SOS) technique, which, in combination with the force theorem, can be used to obtain numerically converged MAE values with appreciably less k points. The MAE values obtained with the SOS technique are supplemented with the result of ''brute force'' total energy calculations on 3.7×10^5 k points. This amount of k points is larger than the k-mesh employed in another recent total energy MAE calculation,[5] yet it might still not be sufficient for attaining converged MAE values. From the obtained MAE values we subsequently address the issue of the capability of the LSDA to describe the MAE's.

As a sort of empirical fact, it was previously discovered that the MAE's calculated with the force theorem depend sensitively on the k mesh, which gave rise to a very poor convergence of the MAE with respect to the mesh size.[3] The source of this poor convergence can be deduced from considering a perturbation theory treatment of the SOC interaction, which is the model underlying the force theorem approach to the MAE. The very first perturbative investigations of the MAE accounted only for the contribution from nondegenerate states,[1,2] but later studies[13,14] and also more recent ones[3] supplied evidence for important contributions also from degenerate states. Degenerate states may occur in two ways: First, spin-degenerate states, i.e., majority and minority spin bands at the Fermi energy, which — in the absence of SOC — cross at certain k points.[13] SOC will lift this degeneracy. The total set of such k points forms a one-dimensional hyperstructure on the Fermi surface. The second kind of degeneracy is the symmetry related degeneracy of bands of one spin type, as occurs, e.g., in fcc Ni for the Γ- L direction.[14] Due to SOC, the originally touching constant energy surfaces become disjunct. The corresponding set of k points at the Fermi level is only zero dimensional, and therefore negligible. As for the spin-degenerate states, it can be shown[15] that their contribution to the MAE of cubic materials is of the same order in the SOC constant ξ as that that of the nondegenerate states,[1,2] namely ξ^4. Thus, even though the spin degeneracies occur only in small portions of the BZ, their contribution is as important as the nondegenerate contribution.[15] Consequently, in order to obtain converged MAE's using an evaluation method based on perturbation theory, these contributions should thus properly be taken into account. From the size of the k-space volume where such degeneracies occur, the homogeneous k-point mesh which would be required can straightforwardly be estimated to be at least 10^7 points (cf. Ref. 3).

Before we outline the SOS technique, we mention that two methods were previously proposed to improve the numerical evaluation of the MAE, the state tracking method,[9] which was employed in combination with the force theorem, and the Gaussian broadening (GB) technique,[5] which was applied to total energy calculations. The latter technique was applied to the MAE of the cubic $3d$ metals, whereas the state tracking technique was applied only to the MAE of monolayers.[9] We shall discuss the GB technique later.

To start with, we define the MAE as the total energy difference for the (001) and (111) magnetization directions, i.e., $\Delta E = E_{(001)} - E_{(111)}$. Through application of the force theorem,[3,16] the MAE can be expressed as the difference of k-space sums over all occupied single-particle energies: $\Delta E = \Sigma_{n\mathbf{k}\mathrm{occ}} E_{n\mathbf{k}}(001) - \Sigma_{n'\mathbf{k}\mathrm{occ}} E'_{n'\mathbf{k}}(111)$. These energies are calculated nonselfconsistently, by adding the SOC term $H_{\mathrm{so}} = \xi(r)\, \boldsymbol{\sigma}\cdot\mathbf{l}$ to the scalar-relativistic one-particle Hamiltonian. The basic idea behind the SOS technique is to employ the perturbation theory result,[1,2,15] which states that the MAE in cubic materials appears only in fourth order in the SOC perturbation, i.e., $\Delta E \sim \xi^4$, where ξ is the radial average of $\xi(r)$ over Bloch wave functions. If we now simply multiply the SOC Hamiltonian with a constant prefactor λ we can write the MAE for two orientations $\mathbf{M}$, $\mathbf{M}'$ of the magnetic moment as

$$\Delta E_{\mathbf{M},\mathbf{M}'} \approx \frac{1}{\lambda^4}\left[\sum_{n\mathbf{k}\,\mathrm{occ}} E_{n\mathbf{k}}(\mathbf{M},\lambda\xi) - \sum_{n'\mathbf{k}\,\mathrm{occ}} E'_{n'\mathbf{k}}(\mathbf{M}',\lambda\xi)\right]. \tag{1}$$

At first sight it might seem that with Eq. (1) nothing is gained over the standard force theorem expression. The gain, however, lies in the fact that a smaller amount of k points suffices to sample over the BZ in the case of an enlarged SOC strength, since those portions in the BZ where, e.g., degeneracies are lifted occur in an enlarged volume. If the lifted degeneracies consisted originally of a one-dimensional hyperstructure on the Fermi surface it will subsequently occur through SOS in a $\sim\lambda^2$ times larger volume, while if the lifted degeneracy was only zero dimensional it occurs in a $\sim\lambda^3$ times larger volume. Thus, instead of increasing the k-point number one can equivalently increase the SOS factor.

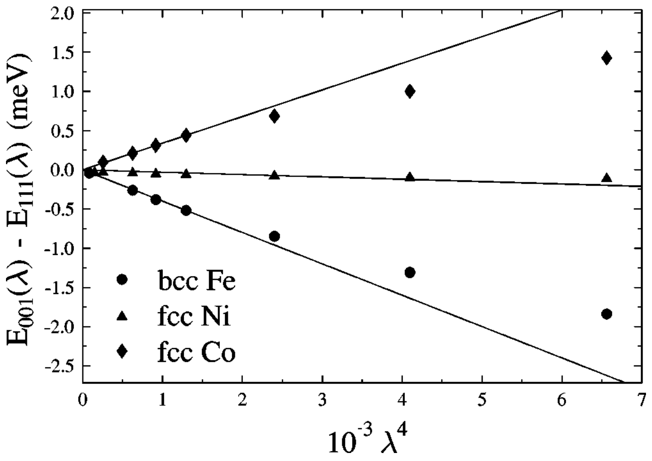

FIG. 1. The SOC scaled MAE's $[=E_{(001)}(\lambda\xi) - E_{(111)}(\lambda\xi)]$ as a function of the SOS factor λ^4 for bcc Fe, fcc Co, and fcc Ni. The solid lines depict the λ^4 dependence.

In the following we first examine the applicability of the SOS technique. To compute the LSDA single-particle energies we use the linear-muffin-tin-orbital (LMTO) method[17] with combined corrections. For the LSDA exchange-correlation potential we have chosen the von Barth–Hedin parametrization.[18] In Fig. 1 we show the SOC scaled MAE's of Fe, Co, and Ni as a function of λ^4 for λ up to 9. The calculations presented in Fig. 1 have been performed on a homogeneous k-point mesh of 3×10^6 points in the whole BZ, using linear tetrahedron integration. We have, furthermore, used a spd basis (i.e., $\ell_{\max}=2$), but we shall address the influence of including f-basis functions below. As can be recognized from Fig. 1, the SOC scaled eigenenergy differences $E_{(001)}(\lambda) - E_{(111)}(\lambda)$ are well described by a linear function of λ^4, which is given by the solid lines. There are, however, two restrictions to be mentioned: First, the λ^4 dependency is fulfilled only up to $\lambda\approx6$. For larger λ's the higher order contributions to the MAE (ξ^6 and higher) are not negligible anymore. Second, the number of 3×10^6 k points is, for small values of λ ($\lambda=$ 1, 2), still rather small for achieving numerically converged MAE's. Therefore, the SOC scaled MAE's for small λ values are less reliable on this k mesh. These restrictions can be regarded obvious. We have, furthermore, verified that for smaller (larger) k meshes larger (smaller) λ's are needed to reach convergence. We therefore conclude that the SOS technique can be applied to achieve converged MAE values within the force theorem. Our calculations in addition demonstrate the perturbation theory result that the MAE scales in lowest order as ξ^4. We mention that scaling of the SOC strength was previously used to show that the magnitude of the magneto-optical Kerr

TABLE I. Calculated MAE's for bcc Fe, fcc Co, and fcc Ni. The MAE is defined as $E_{(001)}-E_{(111)}$ and given in μeV/atom, for the two computational approaches discussed in the text: The SOS technique, for both $\ell_{\max}=2$ and $\ell_{\max}=3$, and straightforward total energy calculations with $\ell_{\max}=3$ on $(72)^3$ k points. Experimental MAE's are those of Refs. 6–8.

MAE	Fe	Co	Ni
SOS ($\ell_{\max}=2$)	-0.4	0.3	-0.03
SOS ($\ell_{\max}=3$)	-0.5	0.3	0.04
Total energy	-2.6	2.4	1.0
Experiment	-1.4[a]	1.3 [b]–1.6 [c]	2.7 [a]

[a] Ref. 6

[b] Ref. 7.

[c] Ref. 8.

effect scales linearly with the SOC.[19] It was also used to show that the MAE of a free standing monolayer is proportional to ξ^2.[9] We emphasize, however, that in the latter case it was *not* applied as a method to improve the k-sum convergence, as is done in the present work.

The force theorem was previously used to compute MAE's by Daalderop *et al.*[3] As a test of our approach, we computed the MAE's of both Fe and Ni, using the force theorem only, for k meshes of size similar to those of Ref. 3. The MAE values we calculated in this manner are quite close to those obtained by Daalderop *et al.*[3] We thus verify the results of Ref. 3 on k-point sets of similar size. To achieve numerically converged MAE's, we applied as a next step the SOS technique. The MAE's are defined by the slope of the solid lines in Fig. 1. The calculated MAE's are summarized in Table I, in which also the experimental MAE's are given. Our converged MAE values obtained for $\ell_{\max}=2$ yield the correct easy axis for Fe and Co, although the computed MAE's are smaller than the experimental ones.[6–8] In the case of Ni, however, the computed MAE for $\ell_{\max}=2$ is very small and with negative sign (-0.03 μeV), in disagreement with experiment. Before this inadequacy in describing the MAE in Ni can be attributed to a failure of the LSDA, the approximations involved in the force theorem and the limited basis set (spd states) have to be investigated. We have tested the latter approximation by including f states in the basis. The results of these calculations are given also in Table I: The inclusion of f states indeed brings the sign of the MAE in Ni in agreement with experiment, but the thus computed MAE is very small, only $+0.04$ μeV. For the calculations including f states we used a k mesh of 2.1×10^6 points, which is, due to computer memory limitations, slightly smaller than the amount achievable without f states. We note that the MAE values of Fe and Co are also minimally changed by less than 0.1μeV through the inclusion of f states. From these results we conclude, first, that f states do not affect the MAE values very much, and second, the SOS technique yields a vanishingly small MAE for Ni.

We have secondly carried out total energy MAE calculations, because the application of the force theorem[3,16] implies several approximations. Especially the fact that the SOC perturbed energies are computed non-self-consistently has been criticized.[9,12] The difference between the self-consistent density calculated with and without SOC may give rise to a contribution of ξ^4 to the MAE, but this is neglected in the force theorem approach.[12] These two methods do thus not necessarily converge to the same MAE value. Self-consistent total energy calculations on a large number of k points are, however, even more restricted by computer limitations than summing single-particle energies. It is, moreover, unlikely that any band structure scheme can provide total energies with an absolute accuracy of less than 1 μeV. One can only speculate that systematic total energy errors will drop out in the MAE. We performed total energy calculations using an $spdf$ basis on a homogeneous k-point mesh of $(72)^3$ ($\approx3.7\times10^5$) points, which was the maximal amount we could achieve. On account of the self-consistency requirement, SOS cannot be combined with total energy calculations. Compared to the much denser k meshes employed in the force theorem SOS approach, this relatively small k-point number could be insufficient. Contrary to the converged MAE's obtained from the SOS method, we can therefore not definitely say that the obtained total energy MAE's are converged with respect to the k-point number. They are, however, converged with respect to the self-consistency requirement, because we carried out self-consistent iterations until stable total energies, having energy fluctuations of less than 0.1 μeV/atom were reached. The results of these calculations are given also in Table I. We note that *our total energy LSDA calculations yield the correct easy axis for all three metals.* Particularly for Ni this is an important finding, since another recent total energy calculation on, however, 10 times less k points yielded the correct easy axis for Fe and Co, but the wrong one for Ni.[5] From Table I we further note that the total energy MAE's are for all three metals larger by 1–2 μeV than those of the SOS method. It thus appears that the approximations involved in the force theorem may influence the MAE value by about 1 μeV, which is of the size of the MAE itself. The total energy MAE's of Fe and Co are ~1 μeV larger than the experimental data, whereas that of Ni is 1.7 μeV *smaller* than experiment. This is an indication that within the LSDA the experimental magnitude of the MAE of Ni cannot be reproduced.

The MAE's of the $3d$ metals were recently evaluated from total energy calculations in which a GB of 0.14–0.20 eV for states close to the Fermi energy was applied to accelerate convergence.[5,20] These calculations were carried out with a full-potential LMTO method, using spd-basis functions and a mesh of about 3×10^4 k points in the whole BZ for Fe and Co, and 4.8×10^4 points for fcc Ni.[5] While the full-potential approach is for many applications better suited than the spherical potential approximation we have used, this is not necessary so for the MAE, because the major contribution of the SOC occurs in the inner atom region, where the potential is approximately spherical (cf. Ref. 3). We have, on the other hand, included f states in the basis, and performed the calculations on a 10 times larger number of points, using the integration scheme of Blöchl *et al.*[21] With the GB technique the correct easy axis was obtained for Fe and Co, but the wrong one for Ni.[5] To understand this, we have also calculated the MAE of Ni using $(36)^3$ ($\approx4.7\times10^4$) k points (and no broadening), which is close to the amount used in Ref. 5. For this amount of k points we also find the wrong easy axis for Ni, consistent with the result of Trygg *et al.*[5] However, our MAE value for $(72)^3$ points shows that it is doubtful that convergence could be achieved on $(36)^3$ points, even in combination with GB. As evidently tiny energy band shapes near the Fermi level are crucially important to the MAE, a rigorous proof seems to be needed that a relatively large GB of these important states will provide the same MAE limit value as that obtained for many k points.

As it previously at first appeared that it might not be possible to describe within the LSDA the correct easy axis or magnitude of the MAE's,[3,5] the orbital polarization (OP) correction[22] to the LSDA has been applied to improve the LSDA MAE's.[23,5] With the OP the correct sign of the MAE was found for hcp Co.[23] It might thus be that application of the OP to Ni could bring the calculated MAE value, which is too small, in better agreement with experiment.

To summarize, we have investigated the ability of LSDA energy band theory to describe the MAE in cubic Fe, Co, and Ni, using two different computational techniques. From numerically converged MAE's, evaluated using the SOS method, and from total energy MAE's, we conclude that for Fe and Co the LSDA unambiguously predicts the easy magnetization axis, whereas the size of the MAE's is only qualitatively reproduced. For fcc Ni we tentatively conclude that the correct easy axis could be attainable within the LSDA, but the absolute value of the MAE deviates notably from experiment. The latter finding is consistent with the well-known fact that the LSDA is less successful in describing Ni than Fe or Co.[24] We find further that the force theorem approach yields MAE's which are systematically smaller in size than those of total energy calculations.

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